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13. ABSTRACT (Maximum 200 words)

High temperature resistant epoxy resins are typically very polar materials and are capable of absorbing considerable quantities of water, typically 1 to 7% by weight. In addition to being very polar, the resulting glassy structures can also be extremely heterogeneous in terms of electron density as a result of the cure process being limited by diffusion. The focus of this work was to quantify this heterogeneous nature in terms of a nanopore content from positron annihilation lifetime spectroscopy (PALS), and then to use this nanoporosity to isolate the topological contributions to the transport process (how much water is absorbed and how fast) from the polar contributions. We demonstrate that if the polarity of the network is maintained constant, the nanopore content does not significantly influence the diffusion coefficient (how fast) but helps dictate the equilibrium moisture uptake (how much). Specifically, it is shown that the ultimate weight gain depends upon the portion of nano-pores that are static as opposed to dynamic in nature. Finally, a simple channel-like morphology of the nanopore structure is introduced to help depict the transport process.

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Moisture Effect in Composites and Structural Adhesives: A Fundamental Study of Underlying Mechanisms

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1. Overview of Results

In research performed in the past 33 months the molecular and nanostructural basis for moisture diffusion in epoxies, and to a smaller extent composites were studied. In this work we quantified the heterogeneous nature of epoxy glasses in terms of a nanopore content using positron annihilation lifetime spectroscopy (PALS). This nanoporosity was then used to differentiate between the polar and topological (the 3-D structure of the network) contributions to the transport process. We showed that if the polarity of the network is maintained constant then the nanopore content has only a mild influence on the diffusion coefficient, but strongly affects the equilibrium moisture uptake. We showed further that the ultimate weight gain depends upon static network defects.

The motivation for this work was the fact that moisture absorption and desorption impair the durability of composites and adhesives based on epoxy resins, and yet the molecular mechanisms of this transport process are only poorly understood. It was hoped that with an improved understanding, users of composites would no longer need to take current material systems and processes as given but instead would be able to tailor them for optimized performance. Another motivation was the distinct possibility that with a better understanding we may be able to have an accurate prediction of durability on the basis of more intelligently designed accelerated aging tests.

In epoxy glasses the molecular packing is quite open and far from perfect because of the 3-D nature of the network. This suggested that water could diffuse in readily. For this to occur, three conditions must be satisfied: 1. The kinetic energy of the water molecule must be sufficient. 2. There must be holes large enough to accommodate at least a single water molecule. 3. These holes must be interconnected, but the channels between the holes, and indeed the holes themselves, need not be permanent. If the holes are static, or "permanent", then the volume fraction of H_2O-sized holes must be very high for percolation to occur. But if the holes are due to density fluctuations and therefore are free to move around (i.e., they are dynamic), then the volume fraction of the correct-sized holes need not be nearly as high, although the diffusivity would presumably still be limited by the volume fraction of holes. This is the reason why it is important to study the size and density of transient (i.e., dynamic) and static holes.

1.1 Characterization of Hole Size and Volume. PALS allows us to study the network topology and make a distinction between dynamic and static holes. PALS is capable of quantifying the size and amount of electron deficient regions between 0.2 to 2 nm in diameter within a dense polymeric solid. When one considers the size of a

water molecule (roughly 0.3 nm in diameter), it is clear why this technique is so appropriate for the moisture diffusion problem. A description of the PALS technique can be found in references [1,2] which also describe a normalization procedure for determining the absolute hole fraction. This procedure involves measuring the macroscopic thermal expansion coefficients near Tg. In this proposal the term "hole" shall be understood to mean those probed by the PALS technique only. In the present context "hole" and "nanopore" are used interchangeably.

If the total hole volume, Vh, of a polymer glass is plotted as a function of temperature, the form of the plot closely resembles a specific volume versus temperature plot. A schematic of this is shown in Fig. 1. If one extrapolates the low temperature hole volume to 0 K, the residual corresponds to the static hole volume, which exists because of the inherently imperfect packing. As the temperature is increased, any additional hole volume created is defined as the dynamic hole volume. To a first approximation, the free volume should be related to the dynamic volume but not the total PALS hole volume, the difference being the static volume, which in thermosets can be quite substantial. In the epoxy resins investigated here, the magnitude of this total nanopore content is typically 3 to 7% by volume in the range from about 0 to 100 deg. C, with approximately 1/2 to 1/3 of this total hole volume being static. This interpretation of course does not preclude the presence of pores greater than 2 nm. Such pores, however, are expected to be so low in volume content in these materials that they would not contribute to diffusion.

1.2   Design of Epoxy Topology. In addition to the hole content, the diffusivity is also affected by the affinity of the diffusant for the host matrix. In the case of water molecules the polar sites in epoxies are expected to attract them. Since our main goal was to study the effect of network topology we needed to maintain a constant matrix polarity in our resins. To neutralize contributions from polar interactions, we studied a series of epoxies where the network topology was systematically altered but the overall polarity (the number of amines) was maintained approximately constant. This series of resins was based on the systems studied by Monnerie, Halary, and co-workers [3,4]. The cross-link density was varied by substituting a mono-amine chain extenders for a diamine cross-linking agent. In order to maintain the affinity of the water for the matrix, the stoichiometric ratio between amine and epoxide was kept constant. Details of this approach and some experimental results are given in an appended progress report. Only a brief summary of the results is presented here.

1.3   Dependence of Diffusivity on Nanopore Content. The results reveal a surprising fact: the rate of moisture transport does not appear to depend on the nanopore content; neither the dynamic, static, nor total nanopore content appears to significantly influence the diffusion coefficient. Furthermore, the diffusion coefficient for each of the resins investigated here appears to be dictated by the glassy state. As long as the material is below its glass transition temperature, the diffusion coefficients of all the materials, from the most rigid to the most flexible, are essentially constant at a given temperature. This is somewhat surprising because in some of the materials, like the most flexible resins, the coefficients are measured at only 10 or 20 °C below their Tg's while for the most rigid systems this is closer to 130 °C below Tg. However one should be aware that the absolute size of the holes in the epoxies investigated is somewhat larger than the static size of a water molecule, so the nanopore volume fraction is primarily a measure of the pore mobility which arises from local segmental motions. Dynamic mechanical results show that regardless of the topology and Tg's, local segmental motions in this series of epoxies all begin at about the same temperature and are fully activated at the temperatures of the diffusion experiments [5]. It is possible then that these results might be different in other types of thermosets where local segmental motions activate at much different temperatures.

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1.4 Dependence of Equilibrium Moisture Uptake on Nanopore Content. A second significant result from this work is the discovery that the equilibrium moisture uptake is proportional to the fractional static hole volume. This correlation is always strongest at lower temperatures and decreases with increasing temperature. This is consistent with the notion that water is capable of plasticizing the matrix and creating new sites to reside at higher temperatures. In contrast to the static hole volume, neither the dynamic nor the total nanopore content correlate in such a simple manner with the equilibrium moisture uptake. We can explain these results in terms of the rigid junctions that are created wherever amine and epoxide groups react. Bond angle restrictions prevent these nanopores from collapsing even at absolute zero. Coincidentally, these are also the locations for hydroxyl groups produced by the amine-epoxide reaction. The more "open" such sites become, the more water can be stored in them. Given the similarity in density between liquid water and cured epoxies, it is not surprising that the weight percentage of water uptake is so similar to the volume percentage of static holes! The ease of opening the "closed" polar sites will also increase with temperature, consistent with the decreased dependence on static hole volumes at higher temperatures.

1.5 Monitoring of Network Development. The extent of cure of a thermoset is conventionally monitored by primary methods such as FTIR, NMR, or DSC. There are also secondary methods – meaning they need calibration by primary methods – such as dielectric spectroscopy, chemorheology, etc. These methods monitor either the progress of chemical reactions or the development of macroscopic properties. None give any direct information regarding the development of the network topology. Yet such information, if available, would be vital for understanding the correlation between the developing network and the ultimate macroscopic properties of interest. We have applied PALS to the characterization of developing networks of a series of tetrafunctional epoxies (TGMDA) cured by DDS subjected to staged curing at successively higher temperatures.

The results on the development of hole size, which is proportional to τ_3, are shown in Fig. 2. These results demonstrate dramatically that increasing the cross-link density as the network cures actually increases the size of the static holes. Upon reflection, this is not surprising because the network acquires an increasingly 3-dimensional character as it cures, whereas a network that has just gelled is more able to collapse, thus screening out the positronium probes. Our experience has shown that the larger static hole size corresponds roughly to larger static hole fraction. This result, when considered along with section **1.4** above, suggests that higher cross-link density should result in a higher level of moisture uptake. (Of course, topology alone does not uniquely define the equilibrium water uptake; network polarity also plays a significant role. If the operation of changing the cross-link density also changes the polar group density, the effect will be convoluted.) The results do suggest that it should be possible to tailor the network structure through a judicious choice of curing agents and curing schedule such that the resulting epoxy network would absorb less water than those currently available. This understanding is particularly advantageous when developing new matrix materials for advanced composites. We shall return to this point when we discuss the specifics of this proposal. We also note that in the latter stages of cure, when the reactions kinetics are slower, it is possible to follow the cure as it occurs in-situ. This is another point to be addressed in the proposed research.

1.6 Comparison between Neat Resin and Composite Results Obtained by PALS. One persistent concern throughout this investigation was the question of whether the PALS results obtained on neat resins have any relevance to composites. In fact, since graphite fibers are free-electron conductors, and the epoxy phase occupies somewhat less than 40% of the volume of the composite, there is a question of whether useful data could be obtained on graphite fiber epoxy composites. This question

was settled by conducting PALS experiments on two composites. One was a boron/epoxy composite (250 ° F cure system) obtained from the AFWL, along with some flash from autoclaving this particular composite panel. The other was a graphite fiber/epoxy composite panel (350 ° F cure system) and its corresponding flash. The reason for studying the flash is to have a control material that is ostensibly the same (composition and thermal history) as the resin in the composite. The results for these two sets of materials are shown in Fig. 3. Except for the high temperature end of the results for the graphite epoxy system, where there appears to be additional curing, the two sets of data are qualitatively the same. They exhibit the same surprising behavior, viz., the flash materials have significantly larger PALS hole sizes than the matrix resins in their corresponding composites. This result is surprising because on the basis of cure shrinkage and constraint arguments, one might expect the matrix resin in the composites to exhibit larger PALS hole sizes because they are presumably under tension. The fact that this was not found to be the case is very perplexing.

The explanation may lie in recent results on thin films of polystyrene. In a NSF-funded study using a mono-energetic beam of positrons to study the surfaces and interfaces of thin polymer films, which we call beam-PALS to distinguish it from the more conventional bulk PALS used in this project, it was found that thin (< 20 nm) thermoplastic films exhibit a considerable constraining effect due to an adhering rigid substrate [6,7]. The constraints are such that very thin polystyrene and polycarbonate films have smaller nanopores than their bulk counterparts at temperatures above the bulk Tg, and, moreover, the strength of the Tg (the change in the thermal expansion coefficient at Tg) is reduced unless the films get considerably thicker. With thermoset networks the constraint might extend farther into the matrix because of the rigidity of the polymer. One might ask what consequence the constraint might have on the composite. A number of possible scenarios come to mind. The constraint could reduce the segmental motions near the fiber surface, assuming the existence of good initial adhesion. This could result in a reduction of the diffusivity, not because of a reduced nanopore size, but rather a lowering of the equivalent temperature. There is already some evidence to support this notion: the diffusivity of composites is higher along the fiber direction than transverse to it [8,9]. (In the transverse direction the diffusion path must include more of the interfacial constrained region.) Another consequence could be a more restricted brittle layer directly adjacent to the surface. The underlying reason is the same as that for the projected change in diffusivity: an equivalent reduction in temperature. However this effect is probably offset somewhat by the shallower stress gradient as a direct result of having a finite interfacial layer. How these two effects might interact with each other is another subject of this proposal. A third consequence might be a reduction in the coefficient of thermal expansion along the fiber/matrix interface. The reduction in the thermal residual stress could have significant effects on interfacial strength.

2. Summary of Accomplishments

2.1   Most significant scientific achievement: Network structure can be optimized to reduce moisture absortion.

2.2   How did we arrived at this conclusion: The molecular and nanostructural basis for moisture diffusion in epoxies, and to a smaller extent composites were studied using positron annihilation lifetime spectroscopy (PALS). PALS is useful for quantifying the size and amont of nanoporosity. We used it to differentiate between the dynamic (molecular motion) and static contributions to the transport process of water in epoxies and composties. Dynamic holes are generated by molecular motion, while static

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holes are generated by inherent network structure resulting from the nature of chemical reactions and reaction kinetics.

The results reveal a surprising fact: the rate of moisture transport does not appear to depend on the nanopore content. Apparently thermally generated holes provide sufficient connectivity because of fluctuation that the hole content does not affect diffusivity of water. But the equilibrium moisture uptake is proportional to the fractional static hole volume. We can explain these results in terms of the rigid junctions that are created wherever amine and epoxide groups react. Bond angle restrictions prevent these nanopores from collapsing even at absolute zero. Coincidentally, these are also the locations for hydroxyl groups produced by the amine-epoxide reaction. This explains the correlation and also suggests that reducing the number of network junctions will reduce moisture uptake, contrary to notions that increasing cross-link density will reduce moisture absorption.

We have also applied PALS to the characterization of developing networks of a series of tetrafunctional epoxies (TGMDA) cured by DDS subjected to staged curing at successively higher temperatures. These results demonstrate dramatically that increasing the cross-link density as the network cures actually increases the size of the static holes. These results also suggest that higher cross-link density should result in a higher level of moisture uptake if the polarity of the network is kept constant. The results do suggest that it should be possible to tailor the network structure through a judicious choice of curing agents and curing schedule such that the resulting epoxy network would absorb less water than those currently available. This understanding is particularly advantageous when developing new matrix materials for advanced composites. We also note that in the latter stages of cure, when the reactions kinetics are slower, it is possible to follow the cure as it occurs in-situ.

2.3   Why is this significant: The materials and curing process can now be selected in a rational way to also improve the moisture resistance of composites. PALS can be used to try out the effects of different curing chemistries and processes.

2.4   Why is this important to the Air Force: Polymer matrix composites and adhesives are used extensively in Air Force systems. These polymers absorb moisture which degrade their performance and durability. The understanding developed will allow the Air Force to improve the performance of these materials.

3. Transition:

We have transitioned the technique and concept of using PALS to monitor cure and environmental degradation processes to Dr. Dave Curliss and Mr. Brett Bolan of the AF Materials Lab. Their addresses are:

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4. References

1. L. Yang, H. Hristov, A. F. Yee, D. W. Gidley, D. Bauchiere, J. L. Halary, & L. Monnerie, *Polymer,* **36** (1995) 3997-4003.

2. H. A. Hristov, B. Bolan, A. F. Yee, L. Xie, & D. W. Gidley, *Macromolecules,* **29** (1996) 8507.

3. S. Cukierman, J.- L. Halary, & L. Monnerie, *J. Non Cryst. Solids,* **131** (1991) 898.

4. J. F. Gerard, J. Galy, J. P. Pascault, S. Cukierman, & J.-L. Halary, *Polym. Eng. Sci.,* **31** (1991) 615.

5. J. L. Halary, personal communication, December 1994.

6. L. Xie, G. B. DeMaggio, W. E. Frieze, J. DeVries, D. W. Gidley, H. A. Hristov, & A. F. Yee, *Phys. Rev. Lett.,* **74** (1995) 4974.

7. G. B. DeMaggio, W. E. Frieze, D. W. Gidley, Ming Zhu, H. A. Hristov, & A. F. Yee, *Phys. Rev. Lett.,* **78** (1997) 1524.

8. B. Dewimille & A. R. Bunsell, *J. Phys. D: Appl. Phys.,* **15** (1982) 2070-2091.

9. C.-H. Shen & G. S. Springer, *J. Compos. Mat.,* **10** (1976) 2.
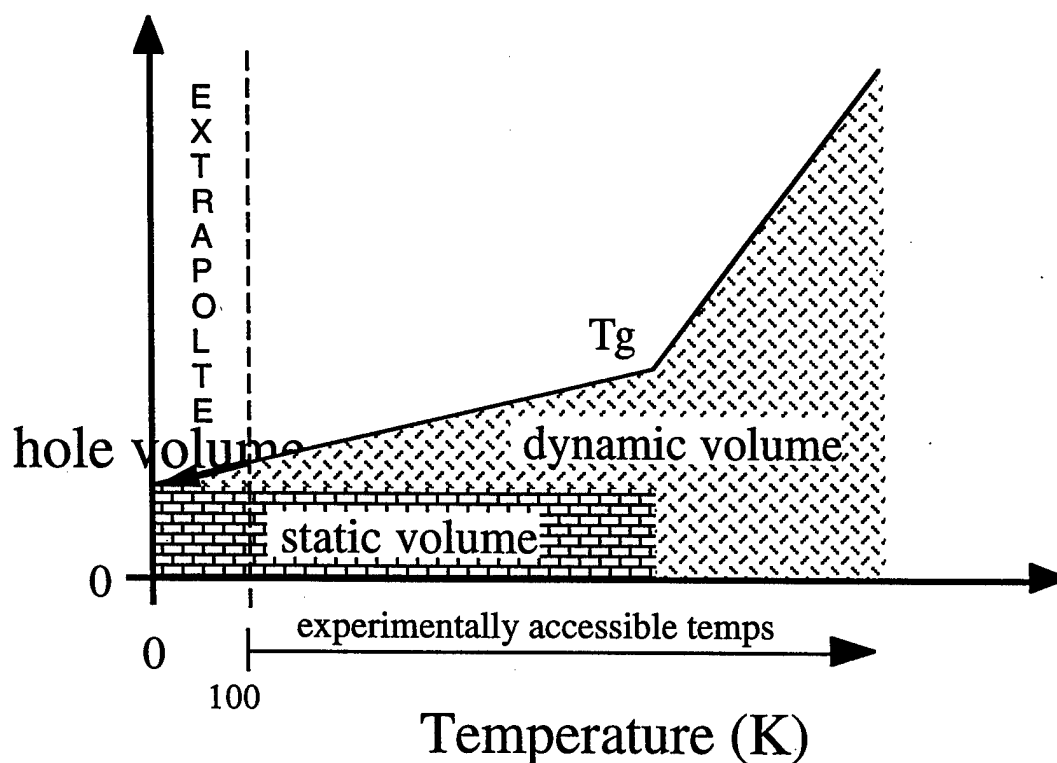
5. Figures

Figure 1. A schematic representation of how the static and dynamic nanopore hole volumes are determined from the total PALS nanopore volume. The total nanopore content is extrapolated from the liquid nitrogen temperature regimes back to absolute zero. The 0 K intercept is defined as the static nanopore volume, with additional thermally generated volume being defined as dynamic.

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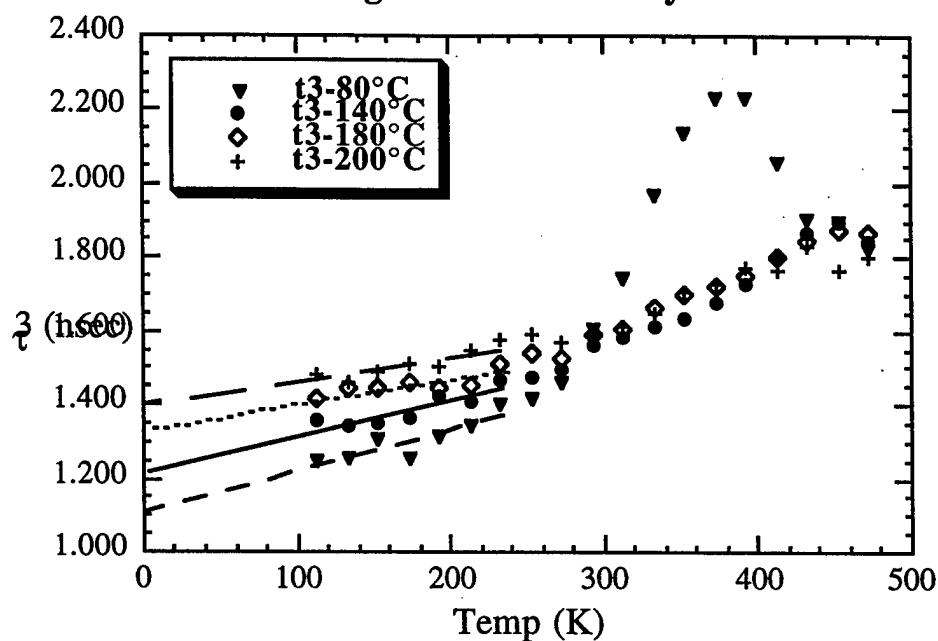**TGMDA-DDS(100)**
Stages in the cure cylce

Figure 2. Stages in the cure cylce for TGMDA-DDS(100) resin sytem. τ_3 -80°C represents the resin which was only cured for 2hrs at 80°C. Each additional step in the curing process has the previous step cured history plus 2hrs at the next specified temperature, i.e. τ_3- 140°C represents the resin which was cured for 2hrs at 80°C and 2hrs at 140°C. Extrapolation of each stage cured resins to 0 K shows that as the network develops larger static hole volumes are the result.

Boron/epoxy composite & flash

(3a)

Carbon/epoxy composite & flash
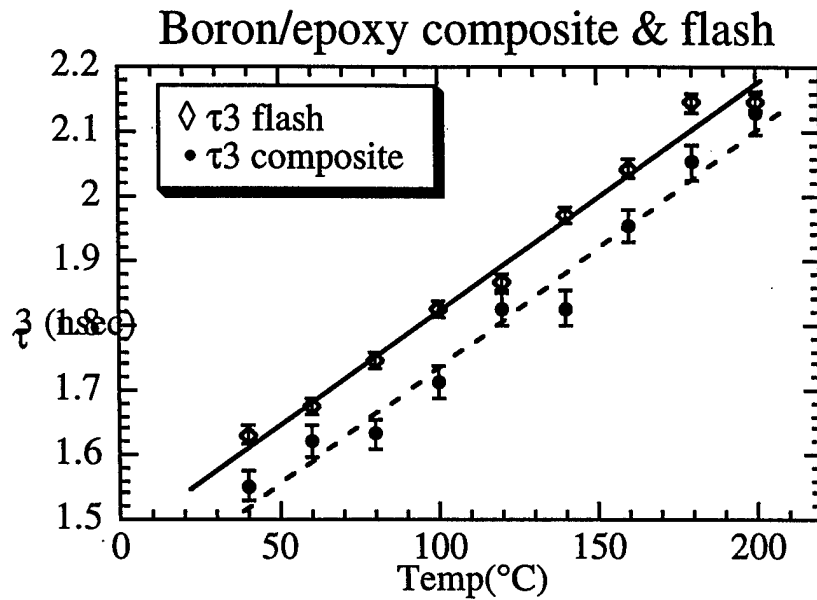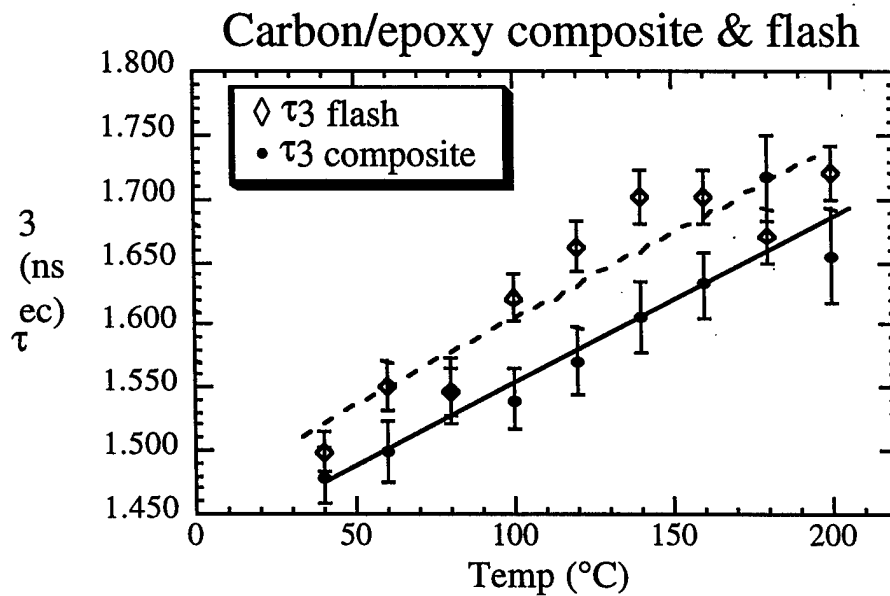
(3b)

Figure 3. Comparison of the τ_3 signal (proportional to hole size) as a function of temperature for a boron/epoxy composite (3a) as compared to a carbon fibre/epoxy composite (3b). In both instances, the confined composite resin has a smaller τ_3 than the neat resin (flash), while both the flash and its respective composite have experienced identical thermal histories.